VEGETATION - ATMOSPHERE INTERACTIONS – THE CRUCIAL ROLE OF TROPOSPHERIC OZONE

Jörg-Peter **Schnitzler**[1] and Yann **Nouvellon**[2]

Vegetation is the dominant source of biogenic volatile organic compounds (bVOCs). On a global scale, the source strengths of bVOCs exceed those of anthropogenic VOCs (aVOCs) by an order of magnitude. Due to their high reactivity, VOCs play important roles in determining atmospheric processes such as secondary organic aerosol (SOA), or when VOCs are in the presence of anthropogenic nitrogen oxides (NO_x), they increase ozone formation and alter the concentrations of hydroxyl radicals, the main atmospheric oxidant. Thus, in changing the oxidative capacity of the troposphere, VOCs influence the local and regional air composition through altering the chemical lifetime of reactive gases with substantial impacts on vegetation and climate.

Biogenic emissions from vegetation are species-specific and the terpenoids isoprene and monoterpenes normally dominate the overall bVOC profile of woody plants. Isoprene and monoterpenes are predominantly emitted in a 'constitutive' manner as a function of light, temperature, and seasonality. In addition to 'constitutive' emissions, significant quantities of 'stress-induced' BVOCs can be emitted into the atmosphere following abiotic (e.g., ozone) and/or biotic (e.g. herbivores) stresses. For instance, some monoterpenoids, the classes of sesquiterpenoids, benzenoids, and volatile lipoxygenase products (so called 'green leaf volatiles') are typically induced and emitted from green foliage after exposure to ozone or herbivores. However, despite the potential of terpenoids and benzoids to influence ozone and SOA formation, stress-induced bVOC fluxes are rarely considered in the context of atmospheric chemistry. In particular the net effect of multiple stress factors, which frequently co-occur in nature, on stress-induced BVOC emission remains still poorly understood.

Besides it's release of VOCs, vegetation also represents a major sink of atmospheric VOC oxidation products, i.e. carbonyls and ketones (i.e. methyl vinyl ketone) challenging the plants' defense system. Thus in anthropogenically polluted urban and suburban areas, the vegetation can suffer

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twice - from the deposition of ozone and from VOC breakdown products generated during ozone formation processes.

The presentation will give an overview on the complexity of biosphere-atmosphere interactions and will highlight future research goals and possible strategies to mitigate harmful atmospheric feedbacks on vegetation.

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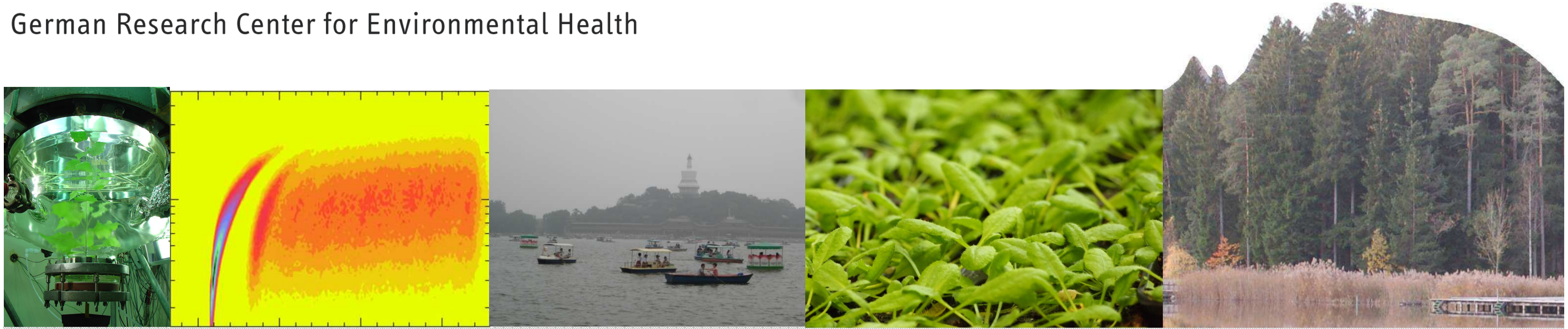

"Vegetation - atmosphere interactions – the crucial role of tropospheric ozone "

Jörg-Peter Schnitzler & Yann Nouvellon

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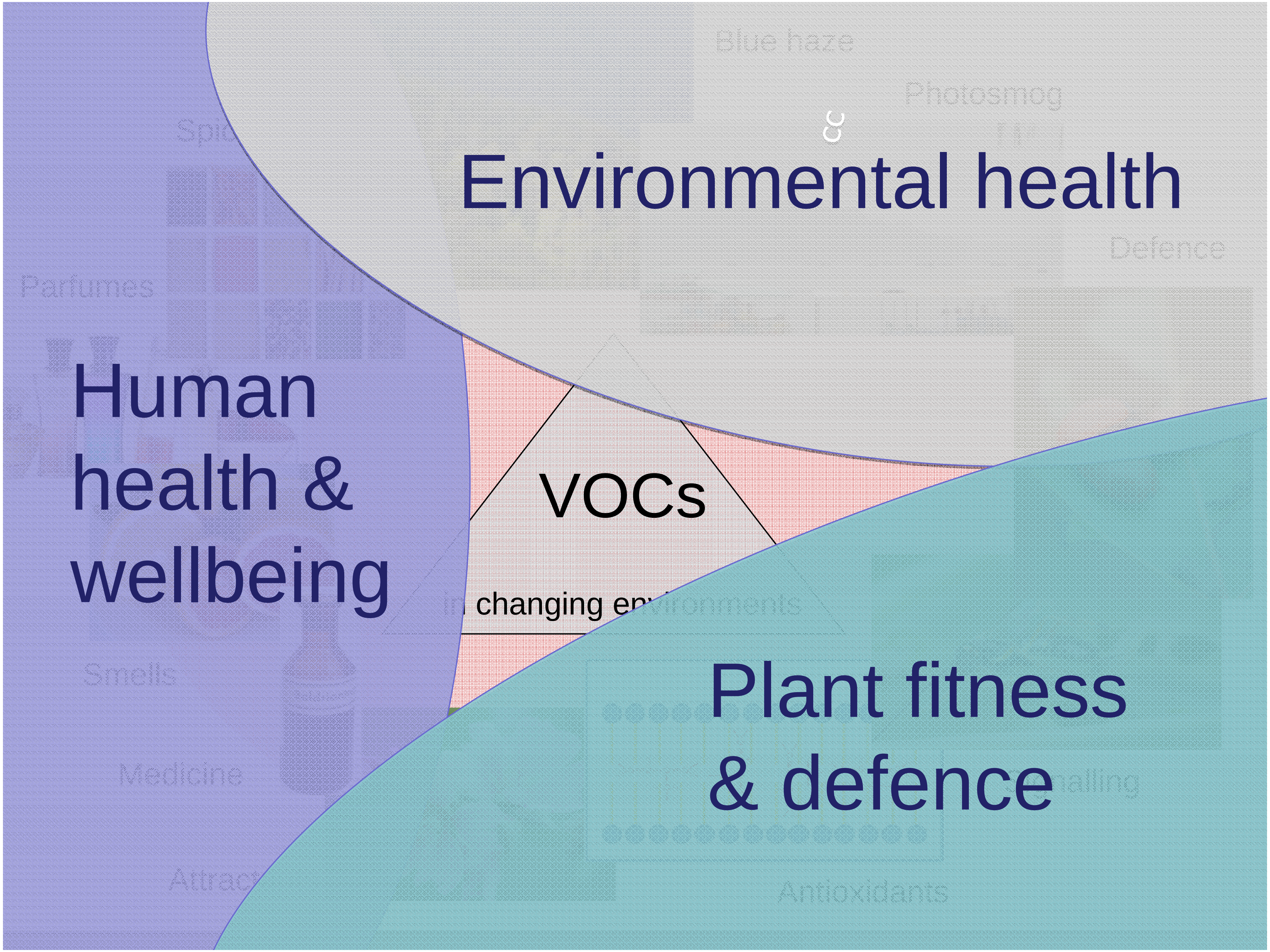
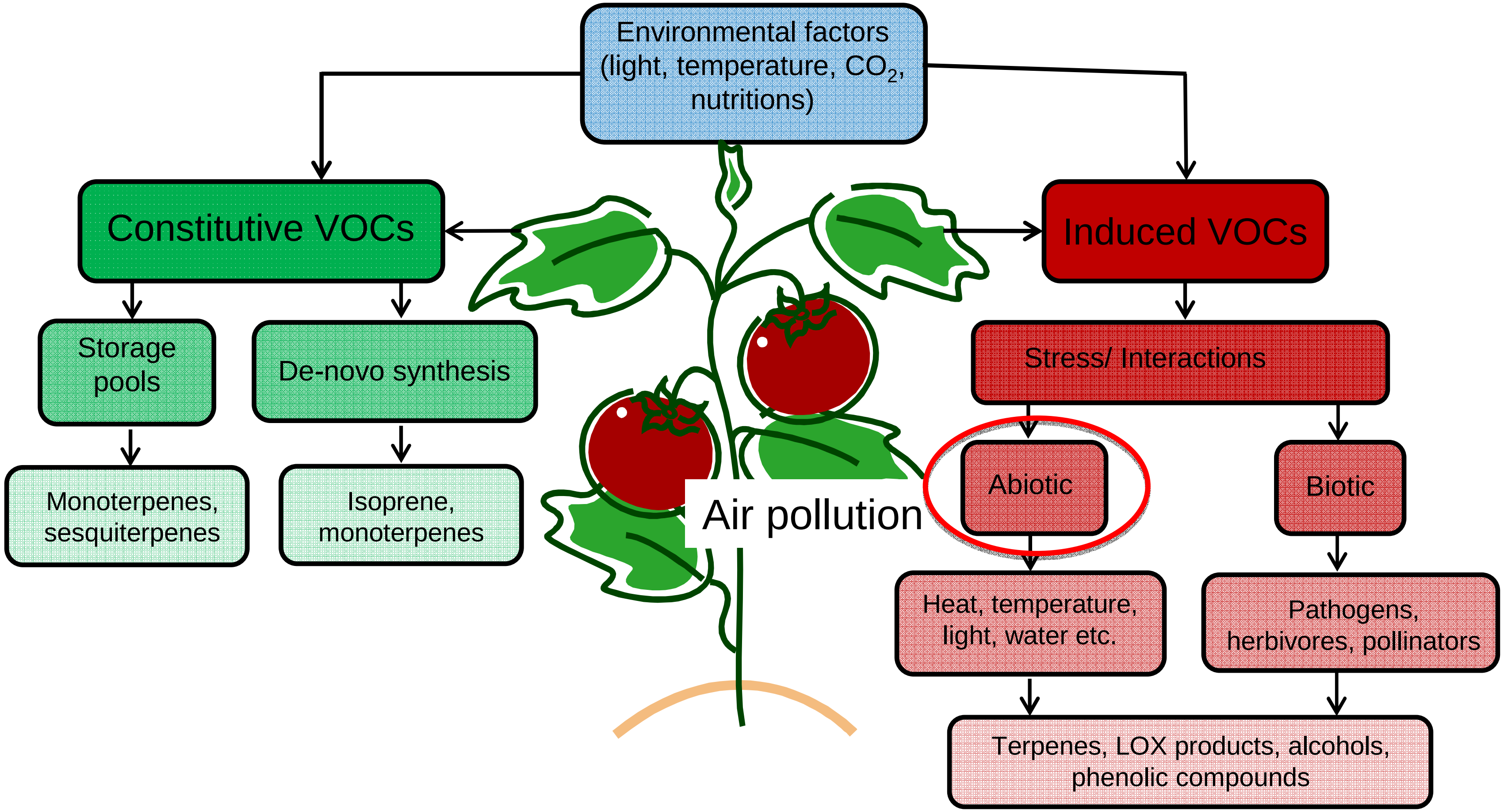
Importance of biogenic volatile organic compounds (bVOCs)


Blue haze
Photosmog
Environmental health
Defence
Parfumes
Human health & wellbeing
VOCs
in changing environments
Smells
Medicine
Plant fitness & defence
Antioxidants

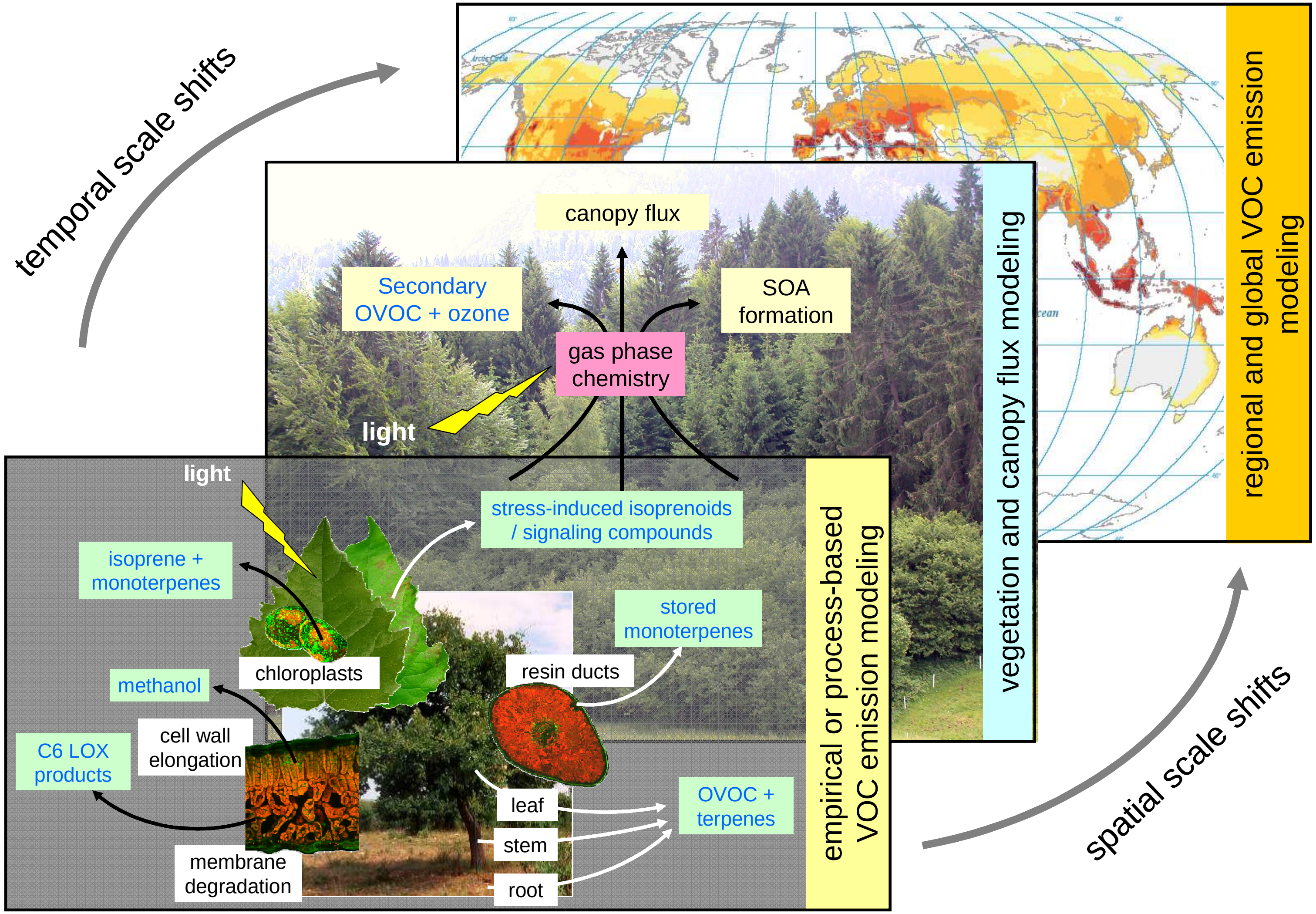
Multiple drivers and sources of plant volatile emissions



Niederbacher et al. (2015) EXB

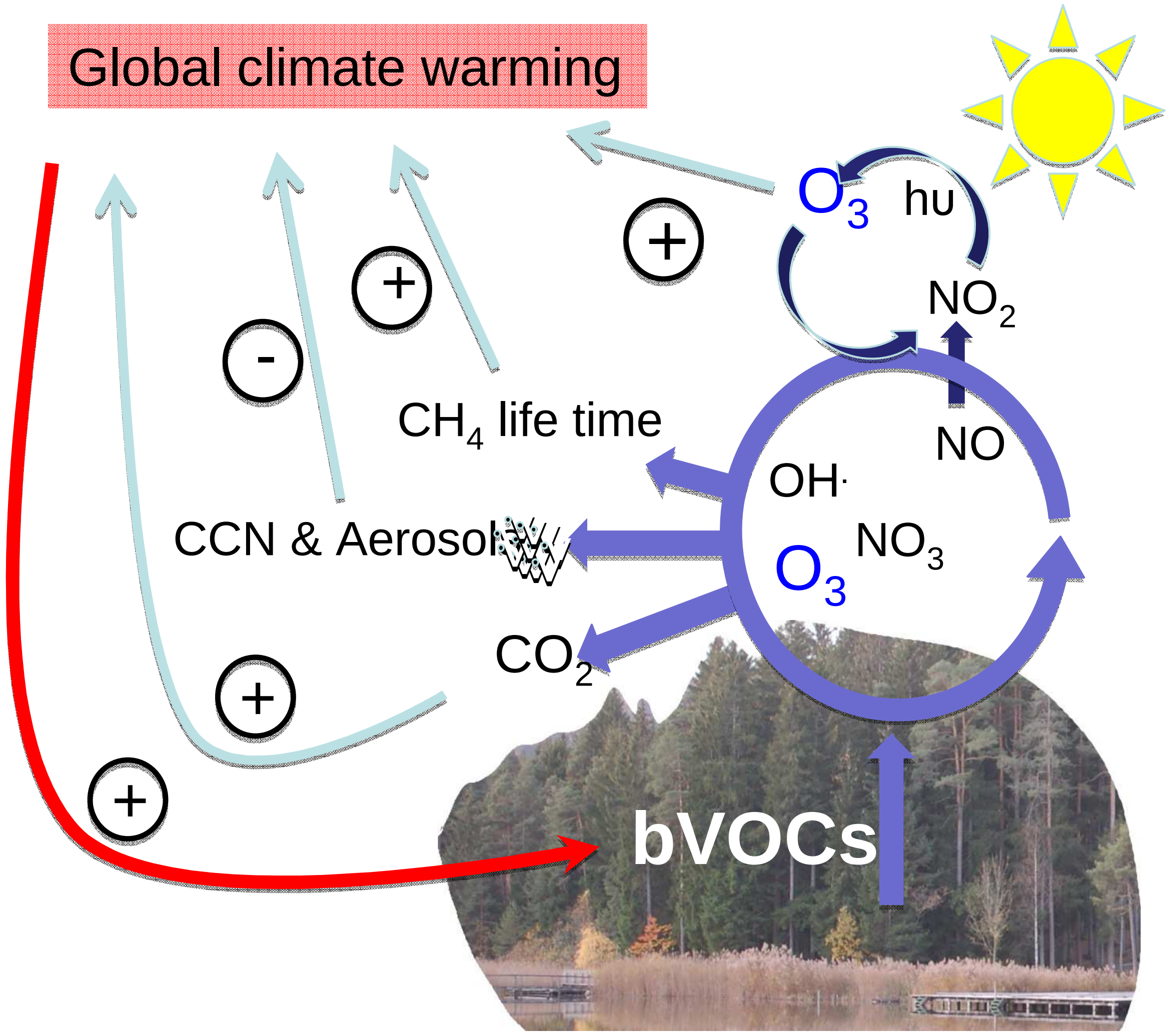
VOCs in air chemistry

Vegetation – Atmosphere Interactions



Loreto et al. (2007) Plant Biology

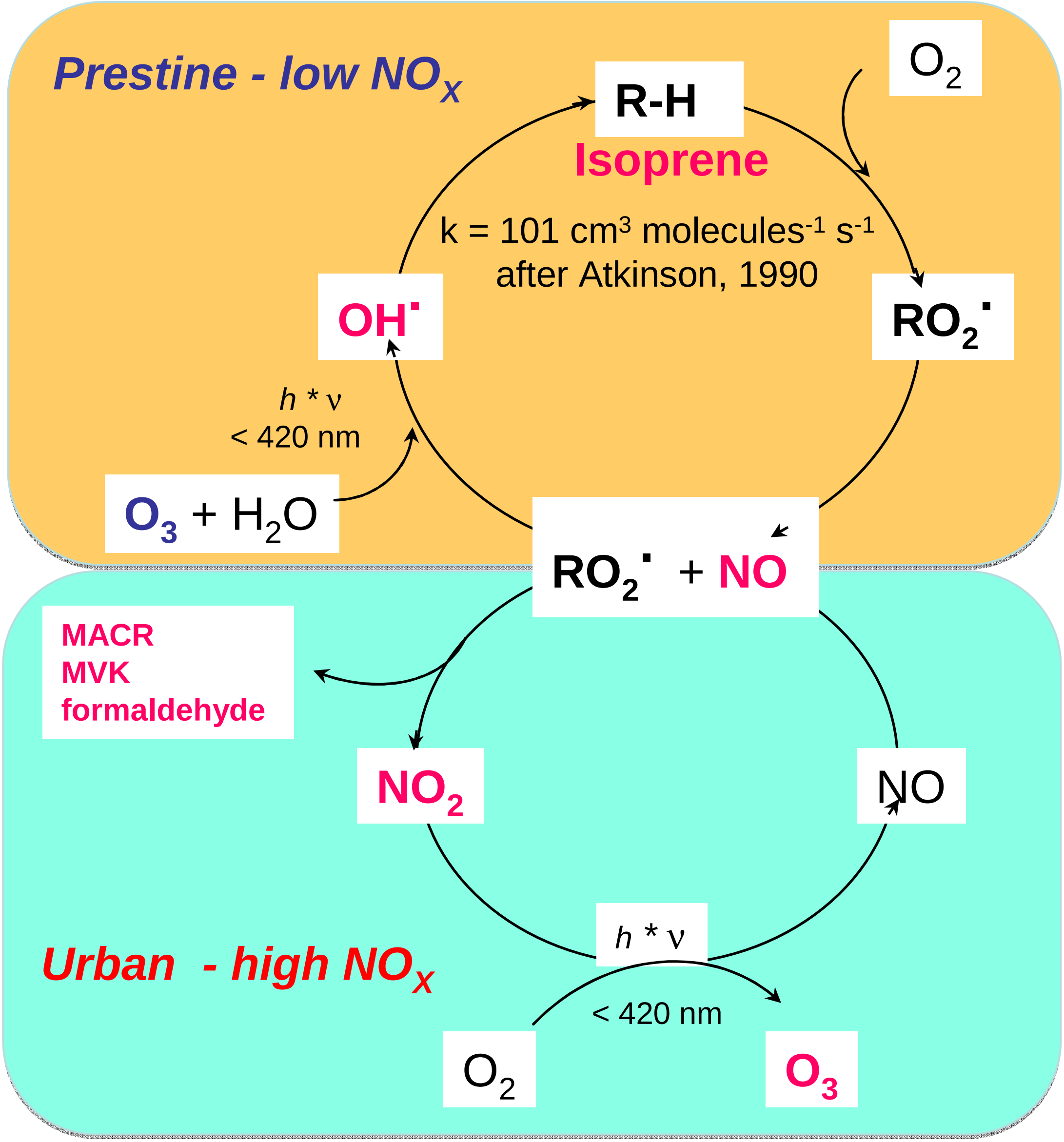
VOCs and their multiple roles in air chemistry



Radical chemistry of ozone / HO· / NOx

Ozone consumption

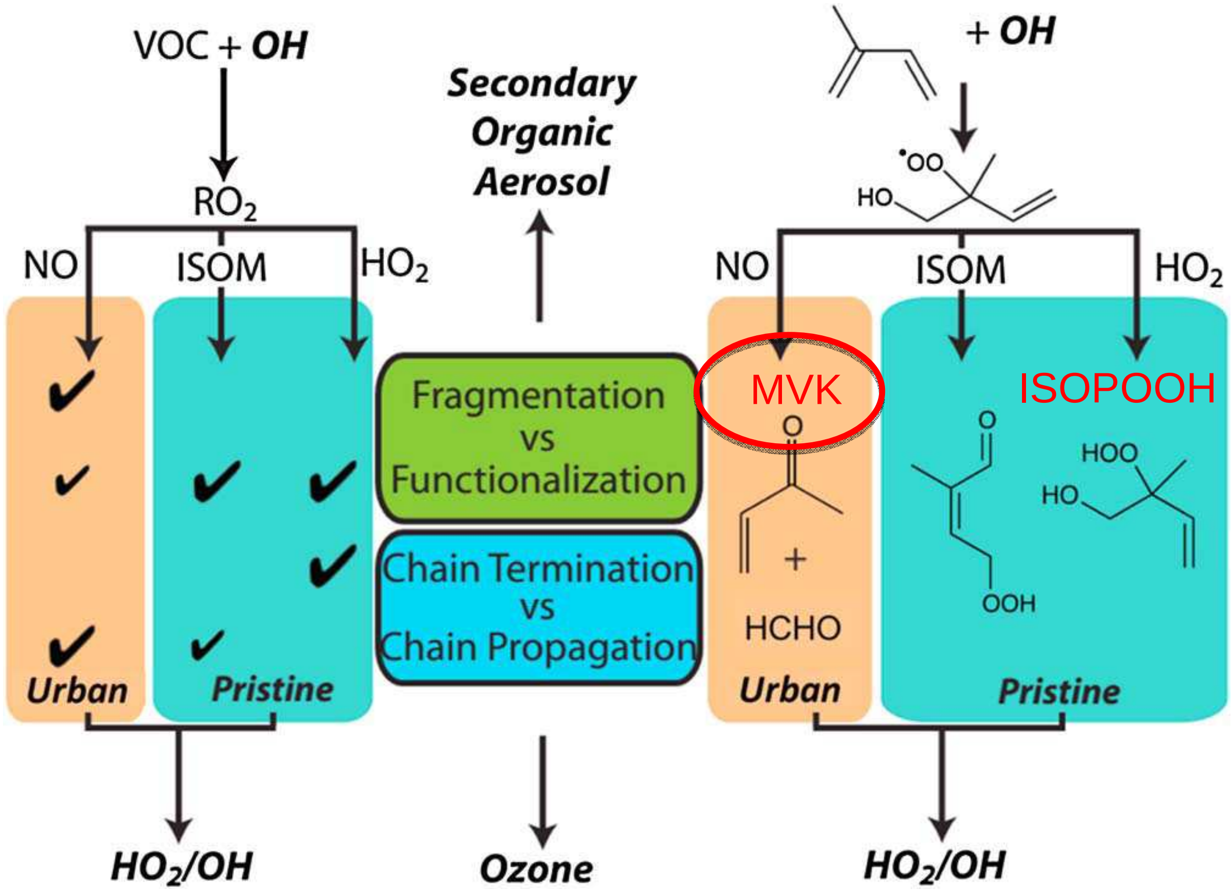
Low SOA formation



High SOA formation

ozone production

Atmospheric VOC oxidation mechanisms under pristine and urban conditions

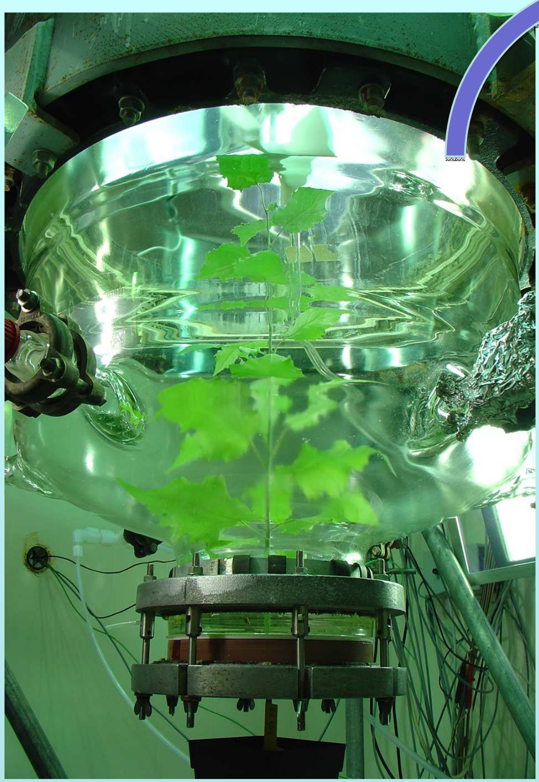


MVK is bioactive/toxic inducing stress responses upon plant deposition

From Rivera-Rio et al. (2014) GRL

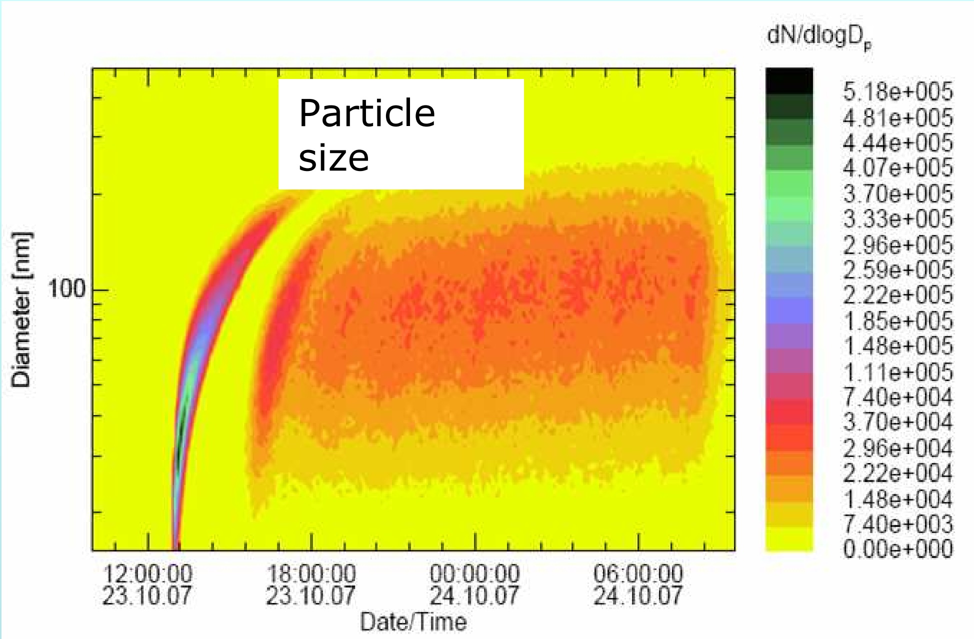
SOA formation from stress-induced poplar VOCs

Plant chamber



Emissions

Reaction chamber

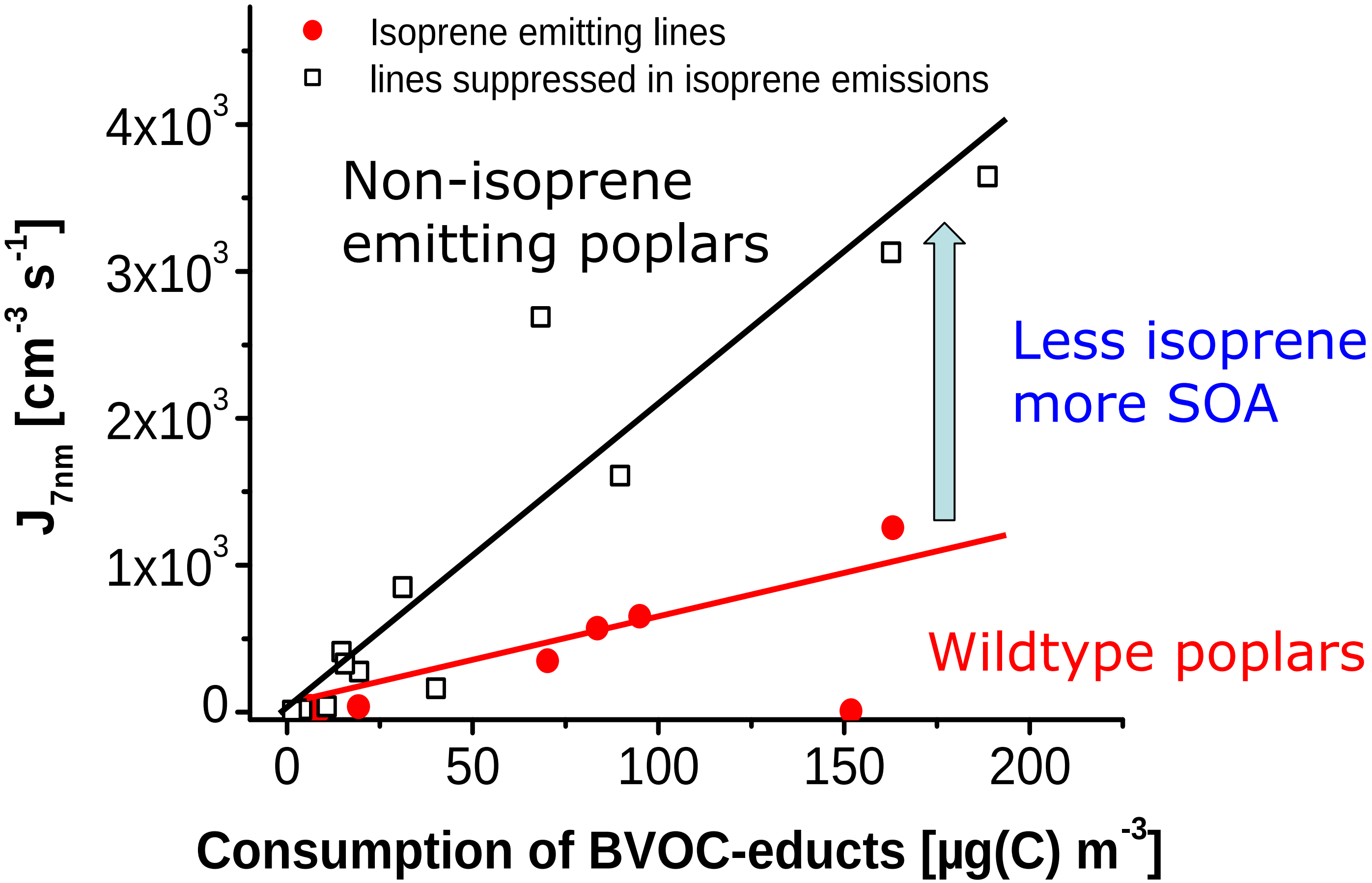


50 ppbv O_3; rH 65%, NO_x-free, plus UV-light

approx. 50 % of VOCs converted to SOA

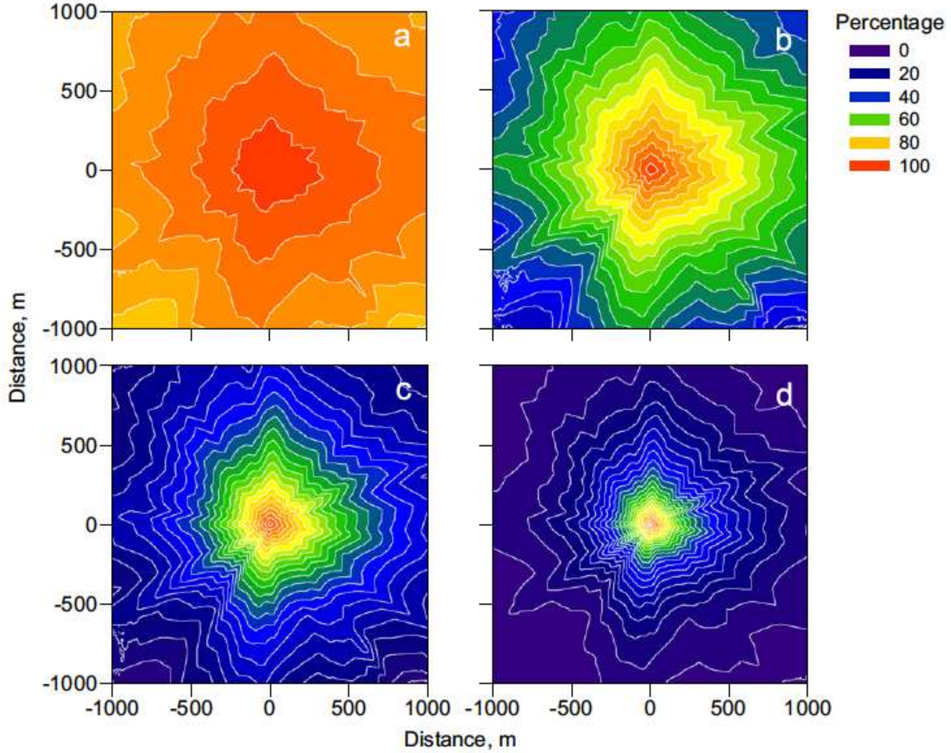
Kiendler-Scharr et al. (2012) ACP

Isoprene's impact on nucleation rates (J7nm) of bVOC (MTs, SQTs, BZs) educts oxidized by OH· and O_3

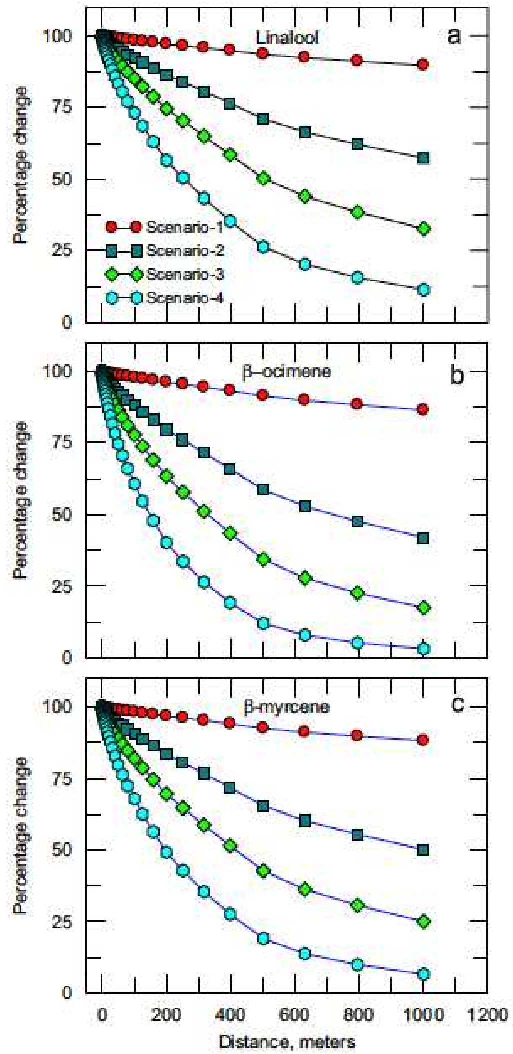


Kiendler-Scharr et al. (2012) ACP

Oxidation of terpenes reduces it’s atmospheric dispersal



Scenario	$[O_3]$ in ppbv	[HO] in pptv	$[NO_3]$ in pptv
I	20	0.02	0
II	40	0.20	1
III	80	0.41	2
IV	120	0.81	5



From McFrederick et al. (2008) Atmos Environ

How does degradation of VOCs influence their biologcal functions?

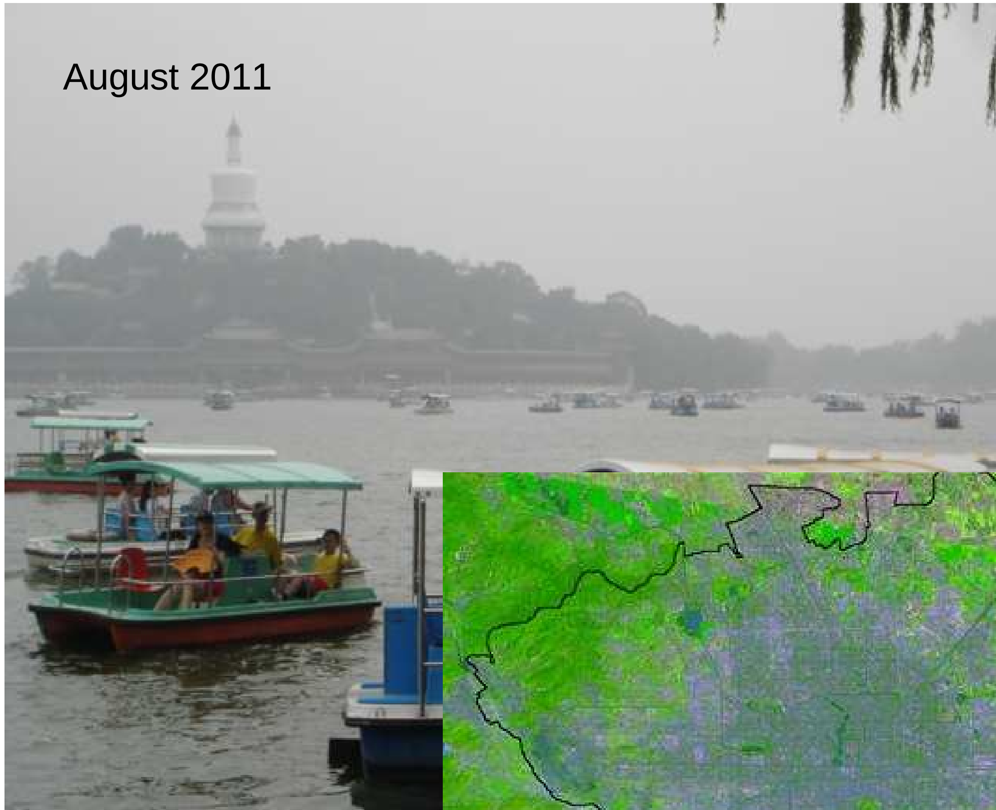
FUNCTIONAL LEVEL	PROCESSES	
ECOSYSTEM Communication with other trophic level	Attract predators Attract parasitoids Deter oviposing herbivores Alarm other plants	Indirect defens e
LEAF SURFACE LEVEL Protect against biotic organisms + harmful gases	Antibacterial & antiungal activitiy Quencing of ozone	Direct defense
TISSUE LEVEL Protect against cellular damage	ROS quenching, antioxidants, protection against high temperatures, signals	

VOCs as markers of environmental stress

VOCs as markers for environmental (urban) stress in a megacity

No.	Species name
1	*Ailanthus altissima* (Mill.) Swingle
2	*Berberis poiretii* Schneid.
3	*Catalpa bungei* C.A. Mey
4	*Diospyros kaki* L.f.
5	*Euonymus japonicas* (Thunb.) cv *microphyllus*
6	*Forsythia ovata* Nakai
7	*Fraxinus velutina* Torr.
8	*Ginko biloba* L.
9	*Koelreuteria paniculata* Laxm.
10	*Ligustrum vicaryi* L.
11	*Liriodendron chinese x tulipikera* (Hemsl.) Sarg.
12	*Lonicera maacki* Maxim.
13	*Magnolia denutata* Desr.
14	*Malus x micromalus* Makino
15	*Plantanus acerifolia* Willd.
16	*Populus tomentosa* Carriere
17	*Prunus cerasifera* Ehrh. cv. atropurpurea
18	*Prunus persica* cv. duplex
19	*Salix babylonica* L.
20	*Sophora janonica* L. (Schott)
21	*Syringa pekinensis* Rupr.
22	*Ulmus pumila* L.

BVOC screening of broad leafed urban tree in Beijing, China

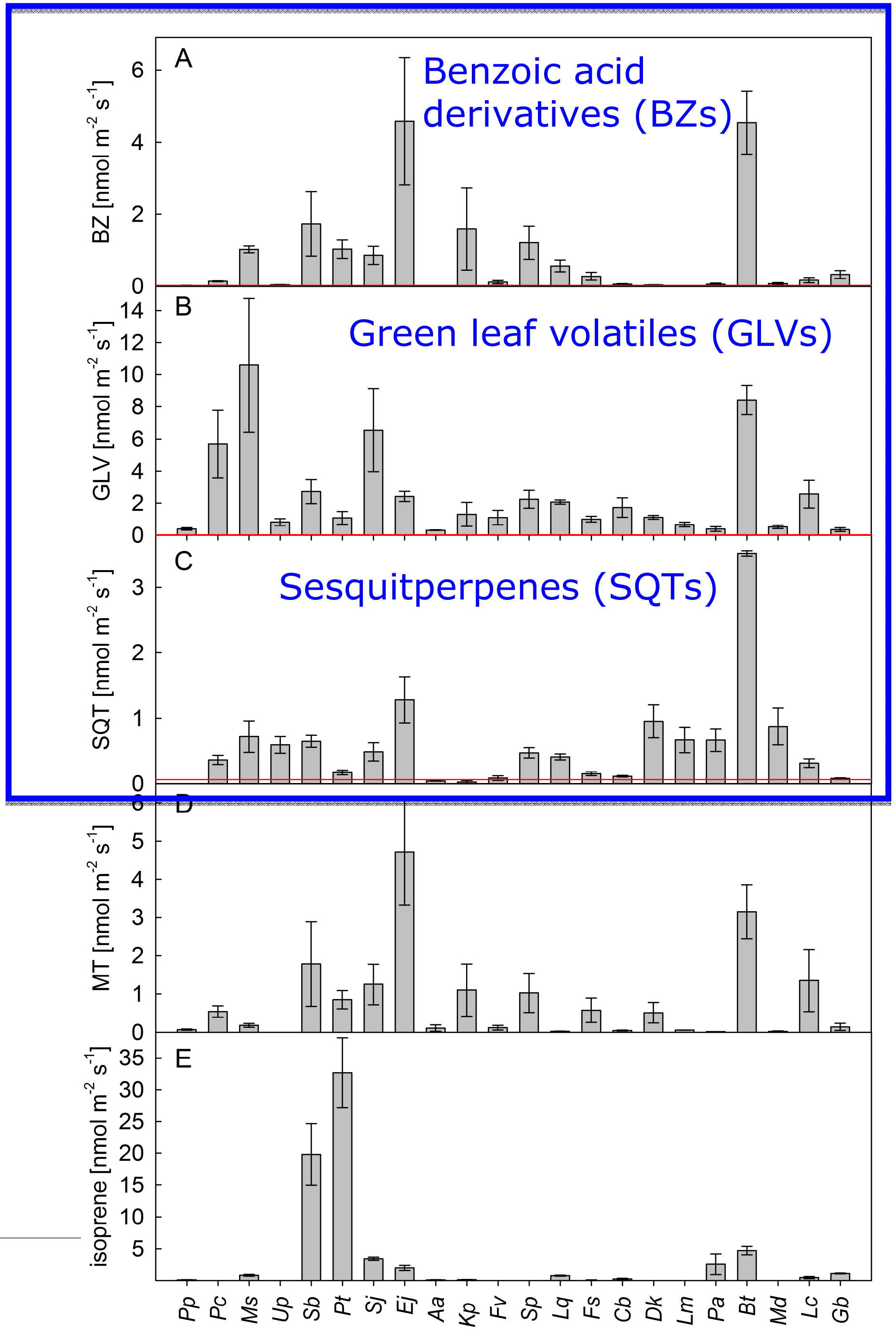


Ghirardo et al. (2016) ACP

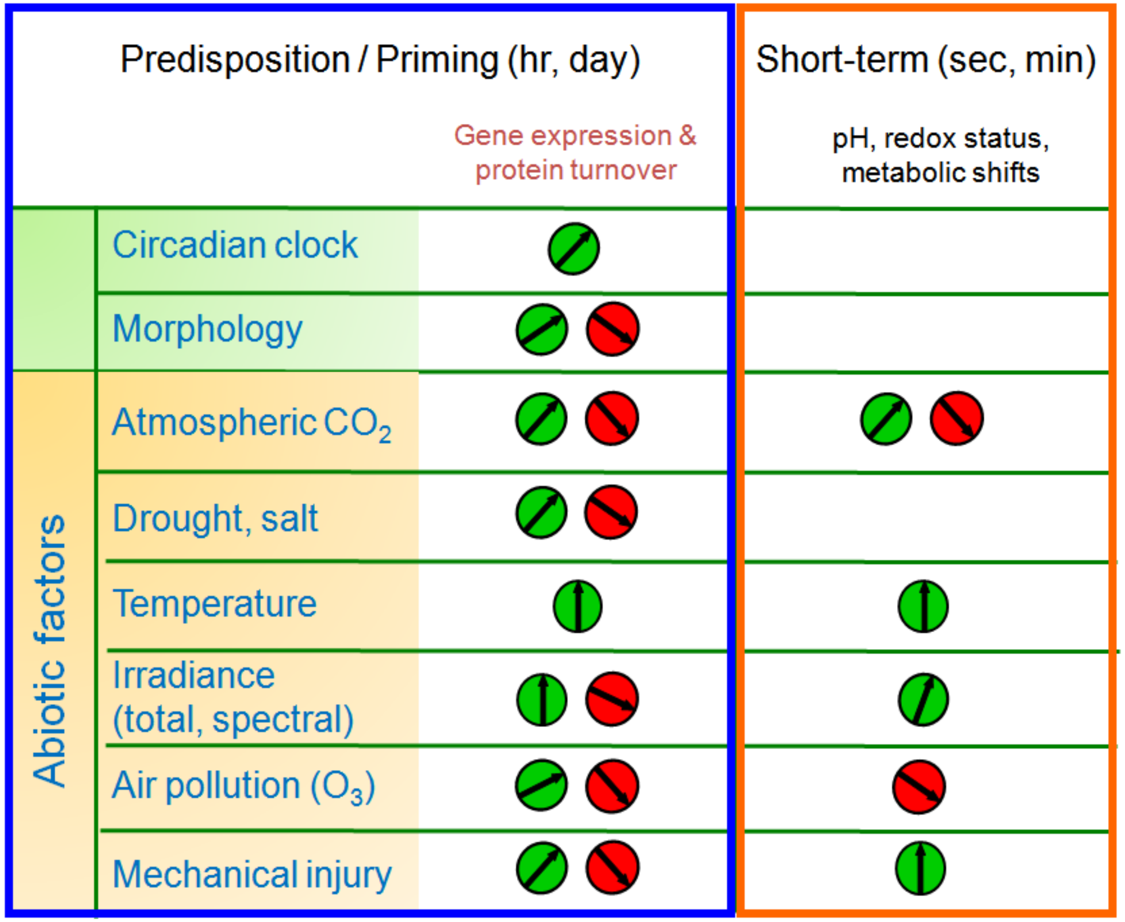
Emission profiles indicative for urban stress

Field campaign in 2011

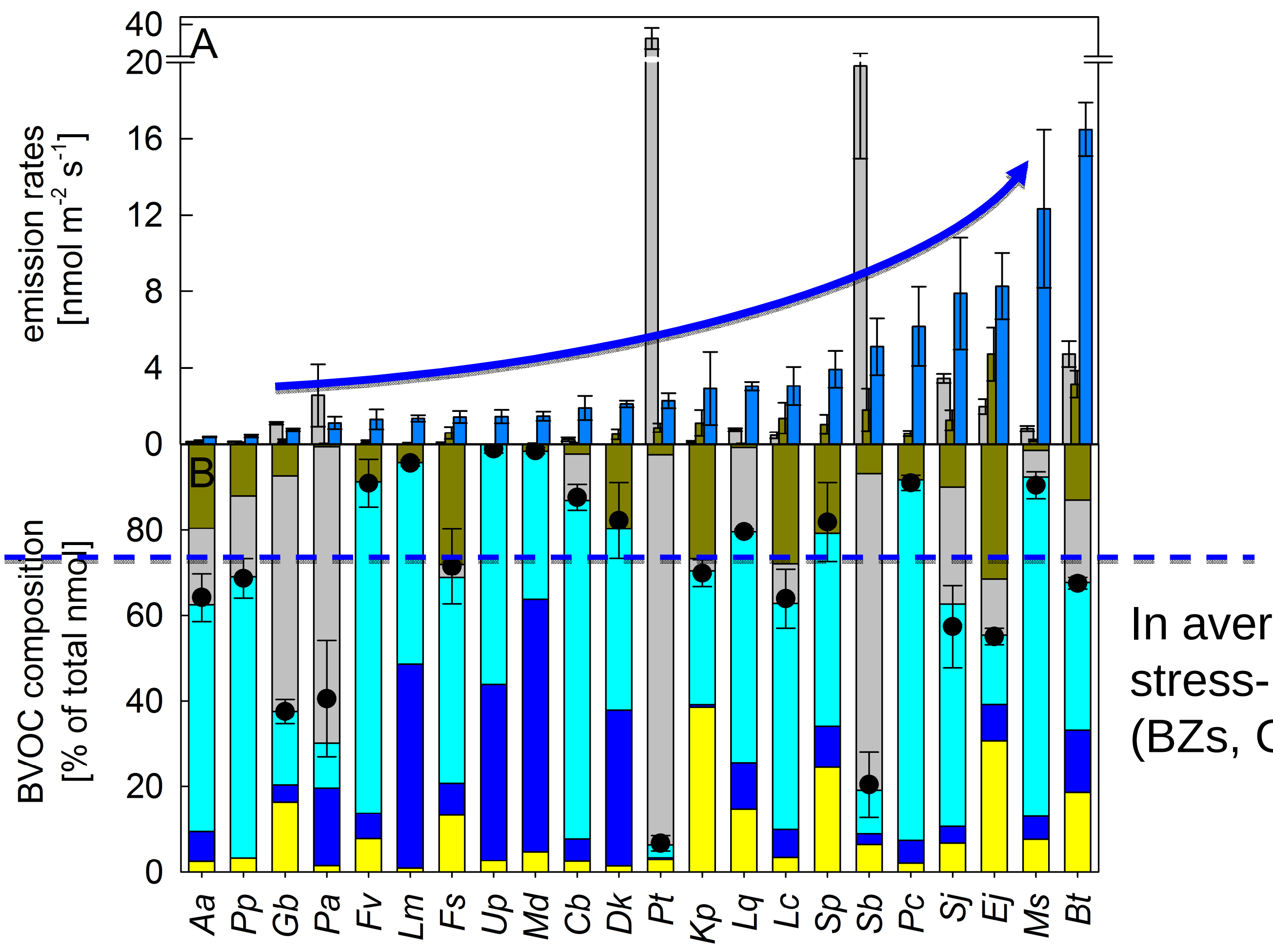
Ghirardo et al. (2016) ACP



Inherent problems in evaluating stress-induced VOC emissions

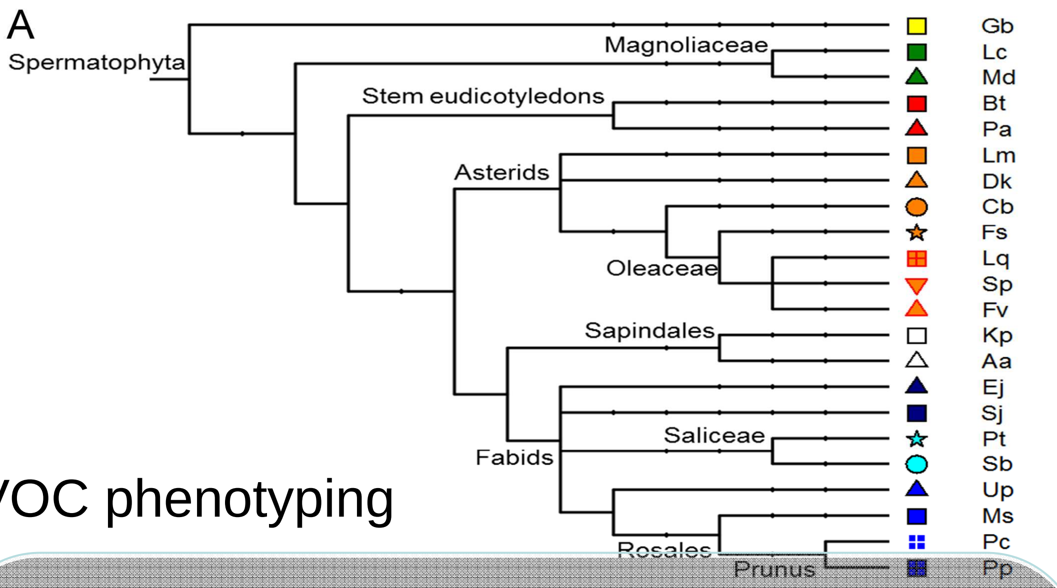


Stress-induced VOCs dominate in many species

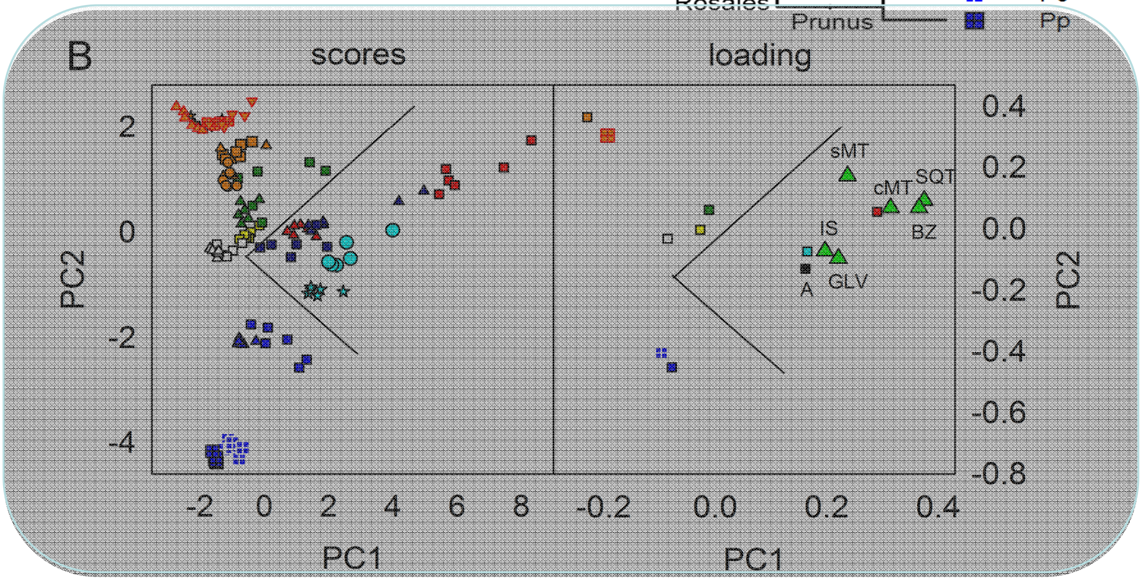


In average c. 75% stress-induced VOCs (BZs, GLVs, SQTs)

Stress-induced VOCs are species-specific



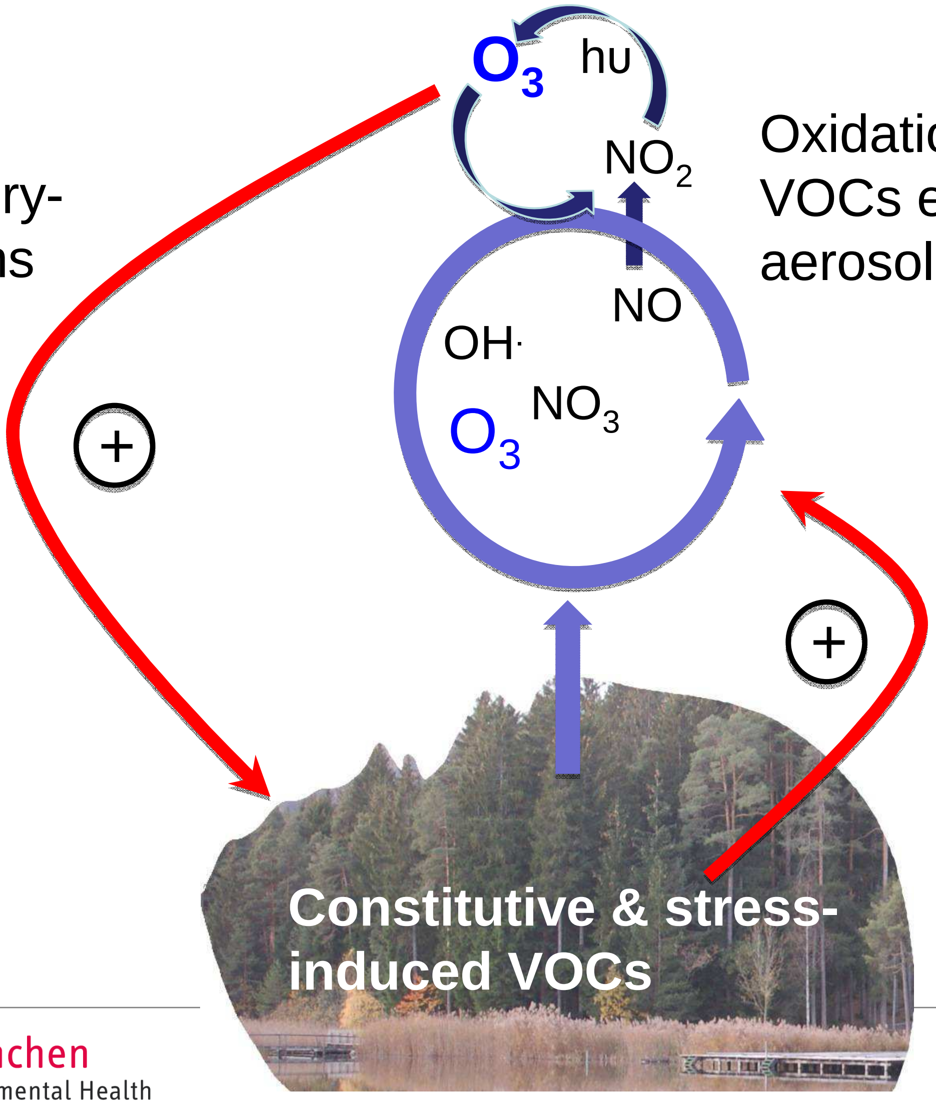
Justification for VOC phenotyping



Ghirardo et al. (2016) ACP

Positive feedback loop of stress-induced bVOCs on photosmog

Air pollution in megacities stimulates herbivory-like VOC emissions



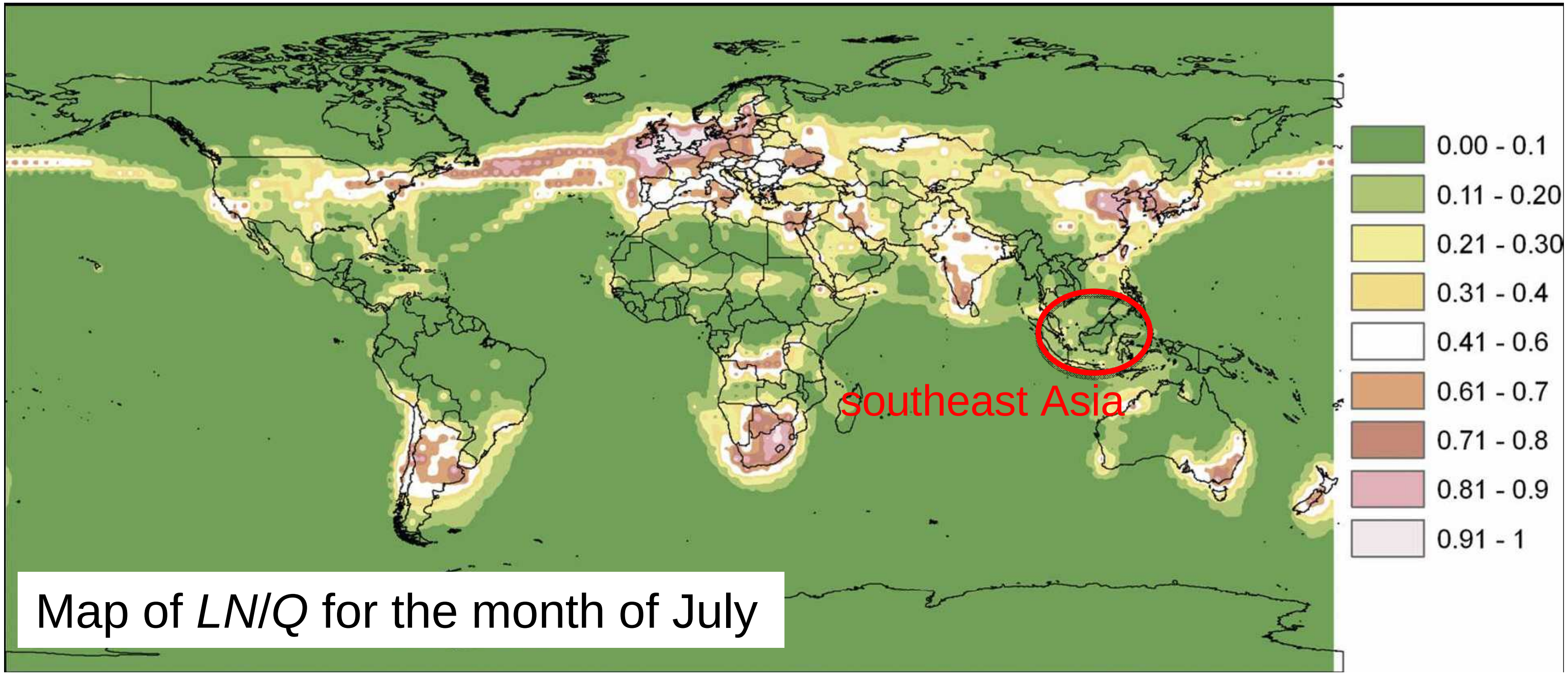
Oxidation of stress-induced VOCs enforces ozone and aerosol formation

Bioenergy plantations and impact on tropospheric ozone formation

Ozone production sensitivity to biogenic VOCs

LN / *Q* ratio:

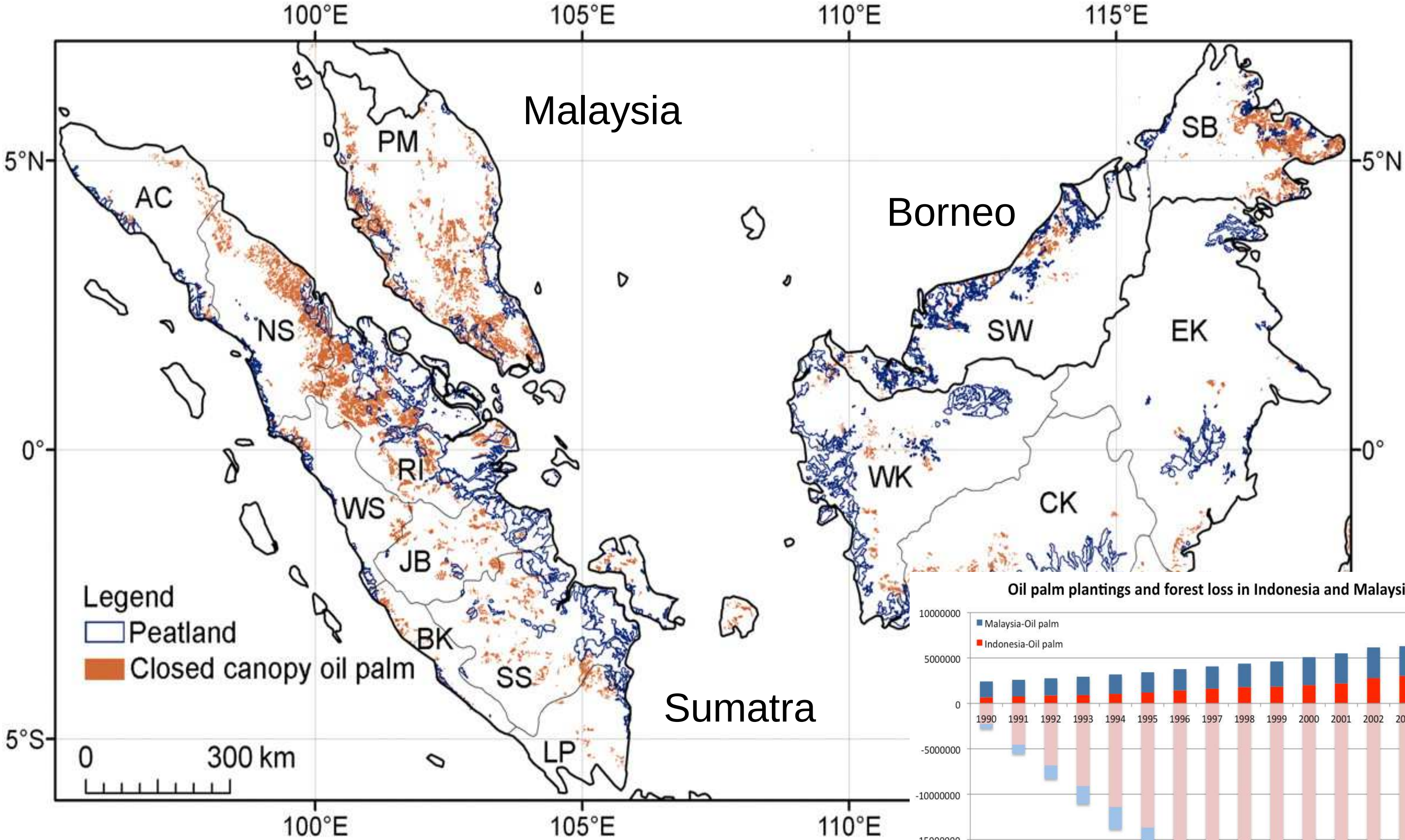
<0.5: O_3 production is sensitive to NO_x
>0.5, O_3 production is sensitive to VOCs

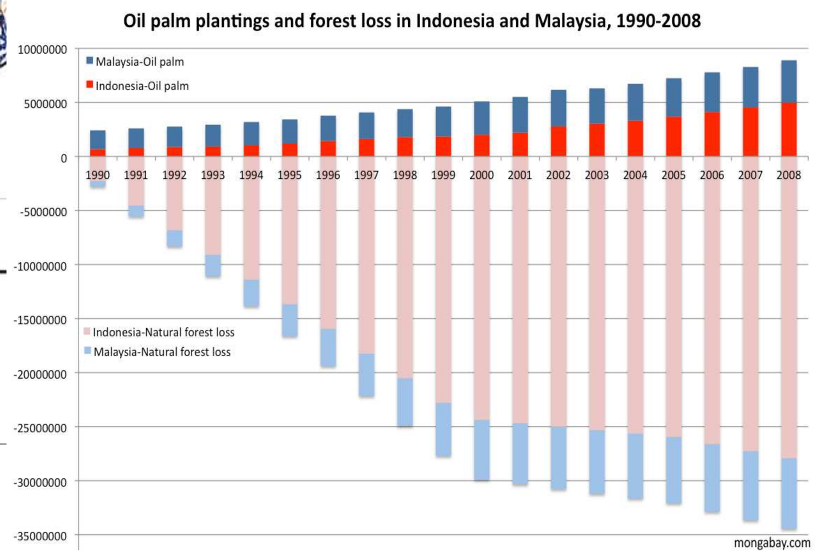


LN: Loss of radicals from reactions with NO/NO_2
Q: sum of radical sinks

From Wiedinmyer et al. (2006) *Earth Interactions* 10, 1-19

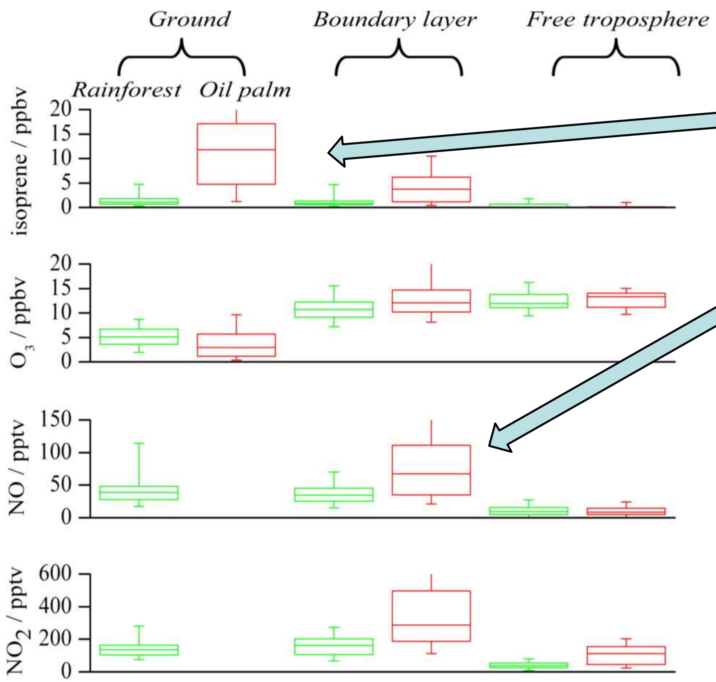
Distribution of oil palm plantations in southeast Asia





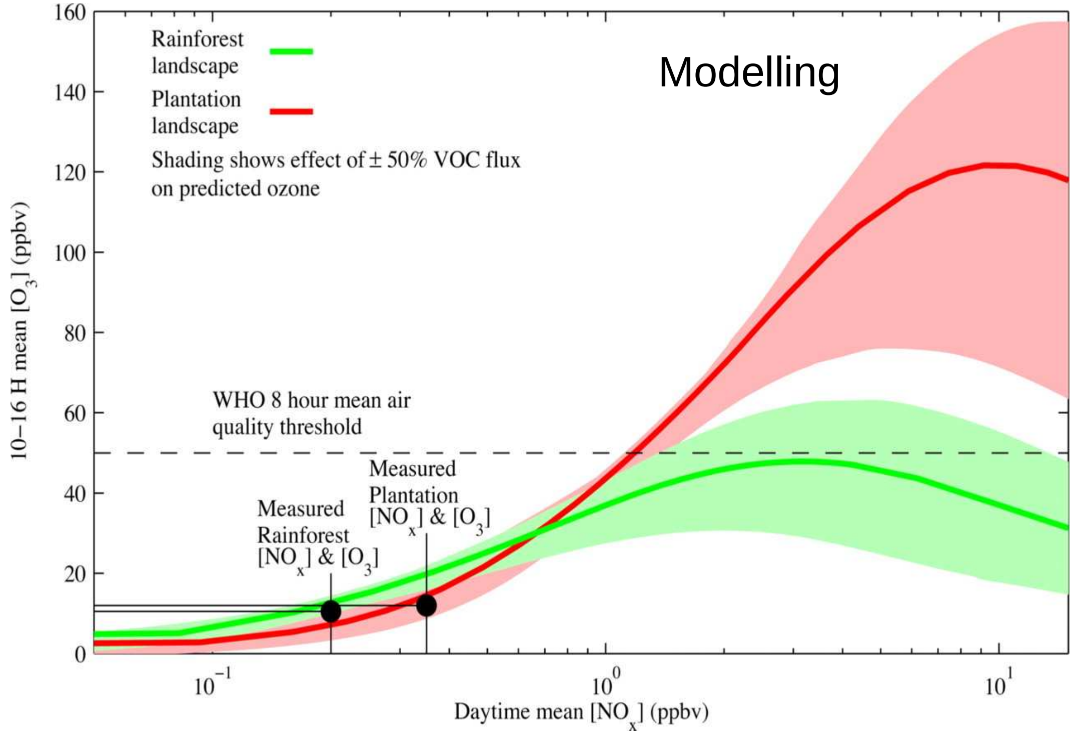
Koh L P et al. PNAS (2011) 108:5127-5132

Ozone formation related to oil palm VOC emissions



Flight measurements

Isoprene and NOx emissions enforce ozone formation



Modelling

Hewitt C N et al. PNAS (2009) 106:18447-18451

Does isoprene impacts human mortality by increase of ozone…..?

nature climate change

LETTERS

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Impacts of biofuel cultivation on mortality and crop yields

Suggestion: SRC plantations in eastern Europe

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Ground-level ozone is a priority air pollutant, causing ~22,000 excess deaths per year in Europe[1], significant reductions in crop yields[2] and loss of biodiversity[3]. It is produced in the troposphere through photochemical reactions involving oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). The biosphere is the main source of VOCs, with an estimated 1,150 TgC yr^{-1} (~90% of total VOC emissions) released from vegetation globally[4]. Isoprene (2-methyl-1,3-butadiene) is the most significant biogenic VOC in terms of mass (around 500 TgC yr^{-1}) and chemical reactivity[4] and plays an important role in the mediation of ground-level ozone concentrations[5]. Concerns about climate change and energy security are driving an aggressive expansion of bioenergy crop production and many of these plant species emit more isoprene than the traditional crops they are replacing. Here we quantify the increases in isoprene emission rates caused by cultivation of 72 Mha of biofuel crops in Europe. We then estimate the resultant changes in ground-level ozone concentrations and the impacts on human mortality and crop yields that these could cause. Our study highlights the need to consider more than simple carbon budgets when considering the cultivation of biofuel feedstock crops for greenhouse-gas mitigation.

turn over these areas from crops, grassland and wasteland within our model vegetation distribution to SRC cultivation. Figure 1a shows the distribution of biofuel feedstock (as a fraction of total vegetation) used in our scenario. These additional SRC crops are projected to provide ~120 Mt yr^{-1} of gasoline equivalent[13], sufficient to meet present EU targets[6].

Effects on ground-level ozone

Planting 72 Mha of SRC species (poplar, willow or eucalyptus) in place of crops, grass or barren ground results in a substantial increase in isoprene emissions (from 11.5 TgC yr^{-1} to 16.0 TgC yr^{-1}), and hence concentrations, across the model domain, shown in Fig. 1b. The spatial distribution of these increases follows the land-use change in Fig. 1a as isoprene has a short atmospheric lifetime (1–3 h). NO_x emissions resulting from fertilizer use are assumed to remain unchanged when food and fodder crops are replaced with biofuel crops[13,14]. The relatively high background levels of NO_x in Europe mean that the rate of photochemical production of ozone is generally limited by the availability of VOCs, with an increase in isoprene emissions leading to enhanced ozone formation[1]. Following SRC planting in the model, annual mean ground-level ozone concentrations increase by an average

Future research questions

On the plant level:

•Understanding the feedback loops of VOC fluxes between vegetation and atmosphere
•Elucidating plant surface VOC-ozone interactions
•Characterising oVOC deposition/detoxification mechanisms

On the vegetation level:

•Understanding the impact of ozone on VOC-based communication (natural and agricultural systems)

On the landscape level:

•Quantifying the impact of bioenergy plantations (i.e. oil palm, eucalypts, poplar) on ozone formation potentials in urban/subrban areas and the tropics